

EVALUATION OF ANTI-FOULING MATERIALS FOR OPTICAL SENSORS

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LONG TERM GOALS

Evaluate biocides and application techniques for optical sensors that will be optically valid and maintenance-free when exposed in marine-estuarine environments for periods ranging from weeks to months. Materials must be cost-effective, clandestine, and exhibit low toxicity directly and indirectly to humans, terrestrial, and marine life.

OBJECTIVES

Identify candidate biocides and obtain commercially available materials. Perform laboratory and littoral exposures with microscopic evaluation of fouling at intervals up to 3 months. Verify optical sensing performance of successful biocide-impregnated/coated candidates from initial exposures. This work is supported by ONR Biological Oceanography.

APPROACH

Commercially available test samples were exposed in natural seawater for up to 3 months with microscopic examination for extent and composition of fouling at intervals. Periodic quantitative and qualitative evaluations of the biofouling were made using environmental scanning electron microscopy (ESEM).

WORK COMPLETED

A Cooperative Research and Development Agreement (CRADA) was established between NRL and Magellan Co., Inc. (1051 Planter Place, Mt. Pleasant, SC) including a no-cost procurement of test coupons coated with chemical formulations for evaluation as antifouling agents. Different formulations incorporated in epoxy resin coatings on glass slides were exposed (as received) in the laboratory to natural Gulf of Mexico/lagoon seawater (salinity 22 ppt) known to contain microorganisms, including sulfate-reducing (10^2 – 10^3), acid-producing (10^3 – 10^4), facultative (10^2 – 10^3) and aerobic bacteria ($>10^4$) per ml sample, in addition to a heavy diatom population. Glass slides were suspended with coated surfaces facing down using a plastic enclosure so as to avoid the surface neuston. Seawater reservoirs were aerated, maintained at

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natural light/dark cycles, and periodically refreshed. Coupons of each formulation were retrieved at 1-, 3-, 7-, 15-, 30-, 60-, 90-, and 120-day intervals and examined using ESEM.

The following commercially prepared formulations provided by Magellan Co., Inc. were evaluated:

- 1) 10,000 ppm zinc pyrithione^{1,2,3} + 300 ppm Vitamin E
- 2) 30,000 ppm oleoresin capsicum^{4,5} + 300 ppm Vitamin E
- 3) 20,000 ppm citricidal^{6,7} + 300 ppm vitamin E
- 4) unknown concentration capsicum^{4,5}
- 5) unknown concentration capsicum^{4,5}
- 6) unnamed coating control (related to samples 4 and 5)
- 7) pre-cleaned glass slide (uncoated)
- 8) Siloxirane® coating control
- 9) unknown concentrations of zinc pyrithione^{1,2,3} and Vitamin E
- 10) unknown concentrations of trichloromelamine,^{8,9} citricidal,^{6,7} Vitamin E
- 11) duplicate of (10) using citric acid^{6,7}
- 12) unknown concentrations of citricidal^{6,7} and Vitamin E
- 13) unknown concentrations of capsicum^{4,5} and Vitamin E

RESULTS

General Observations:

1. Diatoms and clay particles were found on downward surfaces of all test samples at all exposure times. Differences in areal coverage were related to coating composition. In all cases, coatings containing Vitamin E were more effective at retarding settlement/attraction of particulates, including diatoms (Fig. 1).
Once a biofilm has formed, debris, sand, and particulates become entrapped within viscoelastic layers. The influence of electrostatic interactions has been suggested by DiSalvo and Cobet.¹⁰
2. Few bacteria were observed, perhaps due to the predominance of diatoms in the biofilms.
3. Holes and blisters were observed in coatings (1–3) and (5) at 1- to 15-day exposures.
4. Coatings (4–6) disbonded from glass substrata after 30 days.
5. Based on these observations, coatings containing Vitamin E are considered to be the most promising candidates from this series for evaluation in field and optical transmission studies.

IMPACT

The U.S. Navy currently uses a wide range of optical sensors in coastal applications to detect and identify objects within the littoral zone. For example, autonomous unmanned and unmanned underwater vehicles, drifting buoys, mine countermeasure search and destroy devices, bottom-mounted profiling devices, and irradiance chains all have optical sensors that must remain free of fouling for weeks to months. Clandestine data collection in access-denied areas requires similar materials. Blurring and loss of reliably sensed data can seriously impact

interpretation of remote imagery, resulting in failure to detect and discriminate hazardous features for mine

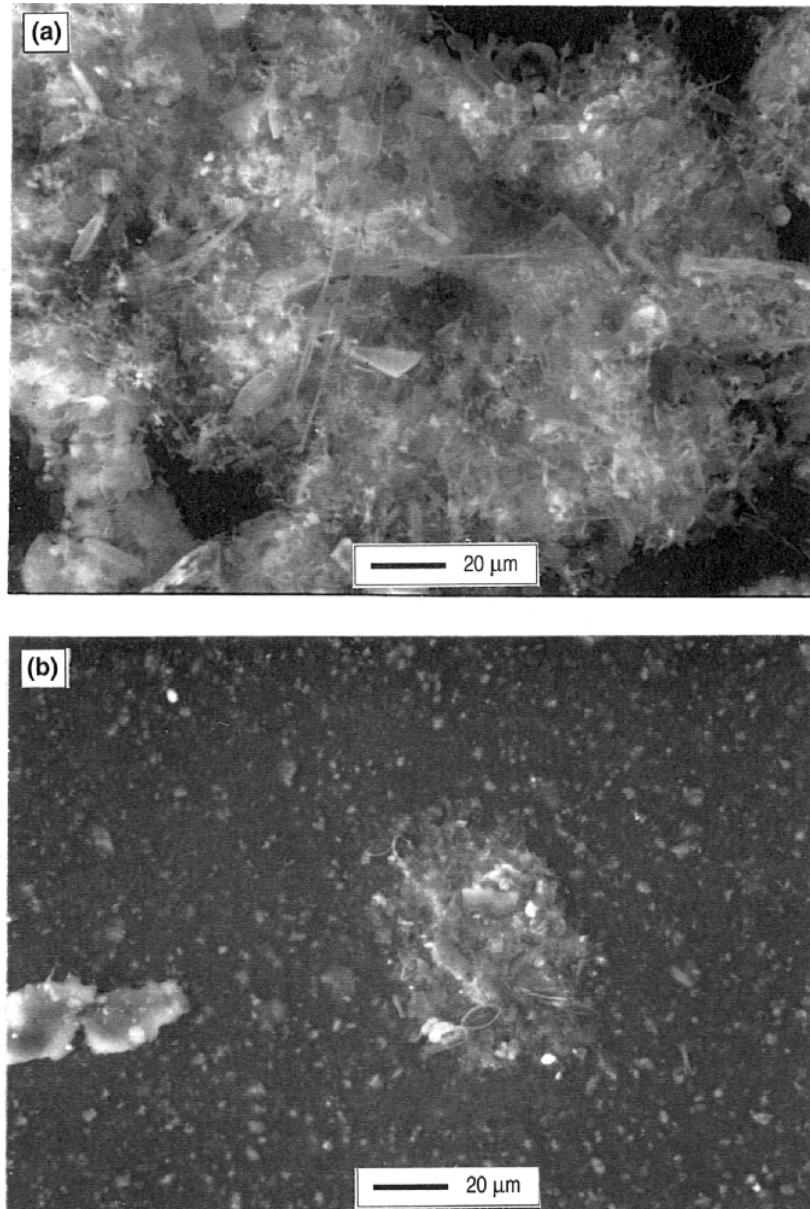


Figure 1. ESEM micrographs showing fouling after 2 weeks exposure to seawater (a) uncoated glass slide and (b) glass slide coated with compound containing Vitamin E.

countermeasures. It is also possible that biocides could be prepared in coating formulations and applied to transducer surfaces to provide short-term fouling protection when ships are in port.

TRANSITIONS

The proposed 3-year project has direct customers in the Mine Killer Program, Magic Lantern, and Magic Lantern-Adaptation (Coastal Systems Station/PMO-210). These projects require optical measurements. From 6.3–6.4, sensory materials will be transitioned to the Tactical Oceanographic Warfare and Support Office for application consideration on unmanned vehicles, towed arrays, or expendable units for environmental characterization.

RELATED PROJECTS

The ongoing and proposed study is an expansion of basic research related to material selection and microbial contamination prevention. The Microbiologically Influenced Corrosion Section is recognized as a center for microfouling studies and routinely receives requests for assistance in the selection of antifouling measures for field applications.

REFERENCES

1. Gavin D. F., Hani R., Waldron C. and Farmer D. A. (1994) Gel-Free Paint Containing Zinc Pyrithione, Cuprous Oxide, and Carboxylic Acid. U.S. Patent 5342437, Olin Corp.
2. Hani R., Waldron C. and Farmer D. A. Jr. (1992) Stabilization of Paints Containing Zinc Pyrithione and Cuprous Oxide Antifouling Agents. U.S. Patent 5098473, Olin Corp.
3. Ruggiero M. A. (1991) Biocidal Paints Containing High Levels of Pyrithione Salts and Copper Salts. U.S. Patent 5057153, Olin Corp.
4. Sagawa S. (1990) Capsium Annum Extract-Containing Antifouling Agents. Japan Patent 90204403, 02204403.
5. Fischer K. J. (1992) Marine Organism Repellent Covering for Protection of Underwater Objects and Method of Applying Same. U.S. Patent 5226380.
6. Bettinger G. E. (1981) Controlling Biological Activity in a Surface Water Reverse Osmosis Plant. *Desalination* 38(1–3): 419–424.
7. Winters H., Isquith I., Arthur W. A. and Mindler A. (1983) Control of Biological Fouling in Seawater Reverse Osmosis Desalination. *Desalination* 47: 233–238.
8. Neal R. L. and Mosher M. W. (1973) Chlorination by Trichloromelamine, an N-Chloroamine. *Proc. W. Va. Acad. Sci.* 45(3): 191–200.
9. Anon. (1969) Sanitizing Solutions. *Fed. Regist.* 34(133): 11543.
10. DiSalvo L.H. and Cobet A.B. (1974) Control of an Estuarine Microfouling Sequence on Optical Surfaces Using Low-Intensity Ultraviolet Irradiation. *Appl. Microbiol.* 27(1): 172–178.